



Zeolite framework stabilized rhodium(0) nanoclusters catalyst for the hydrolysis of ammonia-borane in air: Outstanding catalytic activity, reusability and lifetime

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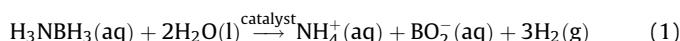
ABSTRACT

Zeolite framework stabilized rhodium(0) nanoclusters were prepared by a two steps procedure: incorporation of Rh³⁺ ions into the Zeolite-Y by ion-exchange followed by in situ reduction of Rh³⁺ ions during the catalytic hydrolysis of ammonia-borane. They are stable enough to be isolated as solid materials and characterized by HRTEM, XPS, XRD, SEM, EDX, and N₂ adsorption. These nanoclusters are isolable, bottleable, redispersible, and reusable as an active catalyst in the hydrolysis of ammonia-borane even at low temperatures. Zeolite framework stabilized rhodium(0) nanoclusters provide exceptional catalytic activity (TOF = 92 mol H₂/mol Rh min) and unprecedented lifetime (TTON = 47200 mol H₂/mol Rh) in the hydrolysis of ammonia-borane at 25 ± 0.1 °C.

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1. Introduction

Since the low density of H₂ makes it difficult to store in compressed or liquid form, storing hydrogen in large quantities is a major hurdle for its widespread usage as an energy carrier [1]. Efficient storage of hydrogen is still one of the key elements of hydrogen economy [2]. Among the new hydrogen storage materials [3], ammonia-borane (H₃N·BH₃, AB) appears to be the most promising solid hydrogen carrier [4] possessing a low molecular weight (30.9 g/mol) and the highest hydrogen content (19.6 wt.%), which is greater than the 2015 target of U.S. Department of Energy (9 wt.% hydrogen for a material to be practically applicable) [5]. AB is nontoxic, stable and environmentally benign, can be handled at room temperature, and can release H₂ either on thermolysis or hydrolysis. The thermal decomposition of AB has been well studied [6]. Recent studies [7] have shown that hydrogen gas can also be generated from the catalytic hydrolysis of AB under mild conditions (Eq. (1)).



Many transition metal catalysts have been tested in the hydrolysis of AB [7,8]. Manners has reported that colloidal Rh(0), Co(0) and Ir(0) catalysts are active in the AB hydrolysis [7b] and among these metals the colloidal Rh(0) in situ formed from the reduction of [(1,5-cod)RhCl]₂ provides the highest activity (turnover frequency, TOF = 900 mol H₂/mol Rh min at 20 °C). However, since the sole stabilizer present in the system is the weakly coordinating chloride anion which cannot provide enough stabilization for the rhodium(0) nanoclusters [9] they retain only 11% of their initial activity in the second run (immediate addition of another batch of AB following the first run gives a TOF value of 100 mol H₂/mol Rh min) and only 1.8% in the fourth run (TOF value decreases down to 17 mol H₂/mol Rh min) as a result of aggregation of the rhodium(0) particles. This study has clearly shown that (i) in the hydrolysis of AB, reducing the particle size of heterogeneous catalyst can provide a significant increase in its activity as the fraction of surface atoms increases with the decreasing particle size [10], (ii) transition metal nanocluster catalysts need to be stabilized to certain extend [11]. Actually, in their catalytic application one of the most important problems is the aggregation of nanoclusters into clumps and ultimately to bulk metal, despite using the best stabilizers [12]. The use of metal nanoclusters as catalysts in systems with confined void spaces such as inside mesoporous and microporous solids appears to be an efficient way of preventing aggregation [13]. As expected, our recent study has shown that the record catalytic activity can be achieved in the hydrolysis of sodium borohydride and benzene hydrogenation

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by intrazeolite ruthenium(0) nanoclusters [14]. Here, we report the exceptional catalytic activity, reusability and lifetime of rhodium(0) nanoclusters stabilized by zeolite framework in the hydrolysis of AB. Zeolite framework stabilized (ZFS) rhodium(0) nanoclusters were easily prepared by a two steps procedure recently reported [14]: ion-exchange of Rh³⁺ ions with the extra framework Na⁺ ions in Zeolite-Y, followed by the reduction of Rh³⁺ ions by AB within the cavities of Zeolite-Y in aqueous solution all at room temperature. They are stable enough for being isolated as solid materials and characterized by HRTEM, XPS, XRD, SEM, EDX, and N₂ adsorption. These nanoclusters are highly active catalyst in the hydrolysis of ammonia-borane even at low temperatures (down to 10 °C). More importantly we have shown that the zeolite framework stabilized rhodium(0) nanoclusters are isolable, bottleable, redispersible, and reusable catalyst in the hydrolysis of ammonia-borane. They retain 70% of their initial activity at the fourth run in the hydrolysis of AB with a complete release of hydrogen.

2. Experimental

2.1. Materials

Rhodium(III) chloride trihydrate (RhCl₃·3H₂O), sodium Zeolite-Y (Na₅₆(AlO₂)₅₆(SiO₂)₁₅₆·xH₂O), sodium borohydride (98%), ammonia-borane (97%), D₂O and BF₃·(C₂H₅)₂O were purchased from Aldrich. Deionized water was distilled by water purification system (Milli-Q System). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C.

2.2. Characterization

The rhodium contents of the zeolite samples were determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy, Leeman-Direct Reading Echelle) after each sample was completely dissolved in the mixture of HNO₃/HCl (1/3 ratio). Powder X-ray diffraction (XRD) patterns were recorded with a MAC Science MXP 3TZ diffractometer using Cu K α radiation (wavelength 1.5406 Å, 40 kV, 55 mA). Transmission electron microscopy (TEM) was performed on a JEM-2010F microscope (JEOL) operating at 200 kV. A small amount of powder sample was placed on the copper grid of the transmission electron microscope. Samples were examined at magnification between 100 and 400 K. Scanning electron microscope (SEM) images were taken using a JEOL JSM-5310LV at 15 kV and 33 Pa in a low-vacuum mode without metal coating on aluminum support. The elemental analysis was performed with an energy dispersive X-ray (EDX) analyzer (KEVEX Delta series) mounted on the Hitachi S-800. The nitrogen adsorption/desorption experiments were carried out at 77 K using a NOVA 3000 series (Quantachrome Instruments) instrument. The sample was outgassed under vacuum at 573 K for 3 h before the adsorption of nitrogen. The XPS analysis performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al K α radiation (1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV). ¹¹B NMR spectra were recorded on a Bruker Avance DPX 400 with an operating frequency of 128.15 MHz for ¹¹B. D₂O and BF₃·(C₂H₅)₂O were used as a lock and an external reference, respectively. At the end of the hydrolysis reaction, the resulting solutions were filtered and the filtrates were collected for ¹¹B NMR analysis.

2.3. Preparation of Rh³⁺-exchanged Zeolite-Y

Zeolite-Y was slurried with 0.1 M NaCl to remove sodium defect sites, washed until free of chloride and calcined in dry

oxygen at 500 °C for 12 h before to use. Rhodium cations were introduced into the Zeolite-Y by ion-exchange [15] of 1000 mg Zeolite-Y in 100 mL aqueous solution of 76 mg RhCl₃·3H₂O for 72 h at room temperature. The sample was then filtered by suction filtration using Whatman-1 filter paper, washed three times with 20 mL of deionized water and the remnant was dried under N₂ gas purging at room temperature for 24 h, then transferred into the drybox (O₂ < 5 ppm, H₂O < 1 ppm).

2.4. Method for testing the catalytic activity of zeolite framework stabilized rhodium(0) nanoclusters formed *in situ* during the hydrolysis of ammonia-borane

The catalytic activity of zeolite framework stabilized rhodium(0) nanoclusters formed *in situ* during the hydrolysis of ammonia-borane was determined by measuring the rate of hydrogen generation. To determine the rate of hydrogen generation the catalytic hydrolysis of ammonia-borane was performed using a Fischer-Porter pressure bottle modified with Swagelock TFE-sealed quick connects and connected to a Omega PX-302 pressure transducer interfaced through an Omega D1131 digital transmitter to a computer using the RS-232 module. The progress of an individual hydrolysis reaction was followed by monitoring the increase of H₂ pressure on Lab View 8.0 program. The pressure versus time data was processed using Microsoft Office Excel 2003 and Origin 7.0 then converted into the proper unit [volume of hydrogen (ml)]. In a typical experiment, 31.8 mg (1 mmol) H₃NBH₃ was dissolved in 10 mL water (corresponding to a maximum amount of 3 mmol = 62 mL H₂ at 25.0 ± 0.1 °C). This solution was transferred with a 50 mL glass-pipette into the FP bottle thermostated at 25.0 ± 0.1 °C. Then, 41.5 mg powder of Rh³⁺-exchanged Zeolite-Y (1.2 wt.% Rh) was transferred into the FP bottle. The experiment was started by closing the FP bottle connected to the pressure transducer and turning on the stirring at 1000 rpm simultaneously. In addition to the volumetric measurement of the hydrogen evolution, in each experiment the conversion of ammonia-borane to ammonium metaborate was also checked by comparing the intensities of signals of ammonia-borane and metaborate anion at δ = -23.9 and 9 ppm, respectively, in the ¹¹B NMR spectra of the solution [8].

2.5. Self-hydrolysis of ammonia-borane

In order to determine the rate of the self-hydrolysis of ammonia-borane in the absence of catalyst, 1 mmol (31.8 mg) H₃NBH₃ was dissolved in 10 mL water and the solution was transferred with a 50 mL pipette into the FP bottle thermostated at 25.0 ± 0.1 °C. The experiment was started by closing the FP bottle and turning on the stirring at 1000 rpm simultaneously. It was found that in the self-hydrolysis of ammonia-borane after one day there is no hydrogen gas generation and additionally ¹¹B NMR spectrum of the resulting solution showed only a signal at δ = -23.9 ppm due to the unreacted ammonia-borane [8].

2.6. Determination of activation energy for the zeolite framework stabilized rhodium(0) nanoclusters catalyzed hydrolysis of ammonia-borane

In a typical experiment, the hydrolysis of 10 mL of 100 mM (31.8 mg) H₃NBH₃ solution catalyzed by zeolite framework stabilized rhodium(0) nanoclusters (36 mg Rh³⁺-Y with a rhodium content of 1.2 wt.%, [Rh] = 0.2 mM) was performed using the method described in Section 2.4 at various temperatures (10, 15, 20, 25 °C) in order to obtain the activation energy (E_a).

2.7. Isolability and reusability of zeolite framework stabilized rhodium(0) nanoclusters catalyst in the hydrolysis of ammonia-borane

After the first run of hydrolysis of 100 mM H_3NBH_3 (31.8 mg in 10 mL), catalyzed by zeolite framework stabilized rhodium(0) nanoclusters (36 mg Rh^{3+} -Y with a rhodium content of 1.2 wt.%, $[\text{Rh}] = 0.2 \text{ mM}$) at 25°C , the catalyst was isolated by vacuum (10^{-3} Torr), and dried under N_2 gas purging at room temperature then bottled under nitrogen atmosphere and transferred into the drybox ($\text{O}_2 < 5 \text{ ppm}$, $\text{H}_2\text{O} < 1 \text{ ppm}$). The isolated and bottled samples of zeolite framework stabilized rhodium(0) nanoclusters were weighted and used again in the hydrolysis of 100 mM H_3NBH_3 after 1, 2 week and 1 month and the results were expressed as turnover frequency (TOF).

2.8. Determination of the catalytic lifetime of zeolite framework stabilized rhodium(0) nanoclusters in the hydrolysis of ammonia-borane

The catalytic lifetime of zeolite framework stabilized rhodium(0) nanoclusters in the hydrolysis of ammonia-borane was determined by measuring the total turnover number (TTN). Such a lifetime experiment was started with a 20 mL solution containing 1.0 mM Rh^{3+} -exchanged Zeolite-Y and 300 mM H_3NBH_3 at $25.0 \pm 0.1^\circ\text{C}$. When the complete conversion is achieved, more ammonia-borane was added and the reaction was continued in this way until no hydrogen gas evolution was observed.

3. Results and discussions

3.1. Preparation and characterization of zeolite framework stabilized rhodium(0) nanoclusters

Zeolite framework stabilized rhodium(0) nanoclusters were prepared by ion-exchange [15] of Rh^{3+} ions with the extra framework Na^+ ions of Zeolite-Y, followed by reduction of the Rh^{3+} ions in the cavities of Zeolite-Y with ammonia-borane in aqueous solution during the hydrolysis of ammonia-borane. Fig. 1 shows XRD patterns of the host material Zeolite-Y, Rh^{3+} -exchanged Zeolite-Y and the zeolite framework stabilized rhodium(0) nanoclusters altogether. A comparison of the XRD patterns clearly shows that the incorporation of rhodium(III) ion into zeolite and the reduction of rhodium(III) ion forming the rhodium(0)

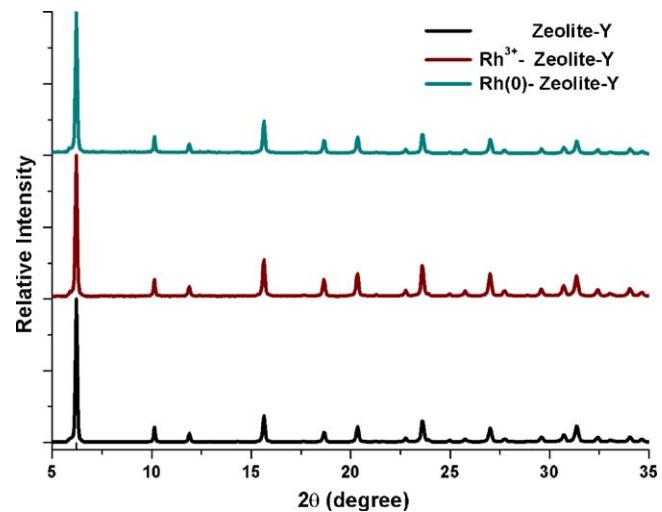


Fig. 1. Powder XRD patterns of the host material Zeolite-Y (Na_{56}Y), Rh^{3+} -exchanged Zeolite-Y and the zeolite framework stabilized rhodium(0) nanoclusters.

nanoclusters cause no observable alteration in the framework lattice and no loss in the crystallinity of Zeolite-Y.

The morphology and composition of zeolite framework stabilized rhodium(0) nanoclusters were investigated by TEM, HRTEM, SEM, EDX and ICP-OES analyses. Fig. 2 shows the SEM images of the zeolite framework stabilized rhodium(0) nanoclusters with a rhodium loading of 1.2 wt.% indicating that (i) there exist only crystals of Zeolite-Y, (ii) there is no bulk metal formed in observable size outside the zeolite crystals, (iii) the method used for the preparation of intrazeolite rhodium(0) nanoclusters does not cause any observable defects in the structure of Zeolite-Y, a fact which is also supported by XRD results, and (iv) rhodium is the only element detected in SEM-EDX spectrum (Fig. 3) of the same sample in addition to the zeolite framework elements (Si, Al, O, Na). Although no bulk rhodium metal is observed outside the zeolite crystals, the SEM-EDX and ICP-OES analyses indicate the presence of rhodium in the samples. Indeed, Fig. 4 depicts the high resolution transmission electron microscopy (HR-TEM) images of the zeolite framework stabilized rhodium(0) nanoclusters with a rhodium loading of 1.2 wt.% in an arbitrary orientation, Fig. 4a, or in a specific orientation, Fig. 4b, suitable for showing the distribution of rhodium(0) nanoclusters in the highly ordered

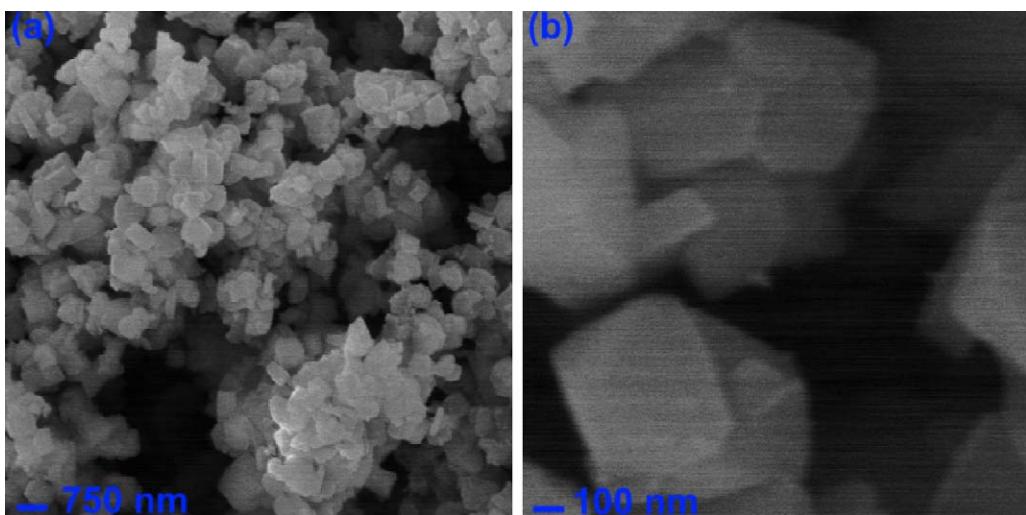


Fig. 2. SEM images of the zeolite framework stabilized rhodium(0) nanoclusters with a rhodium loading of 1.2 wt.% taken at different magnifications.

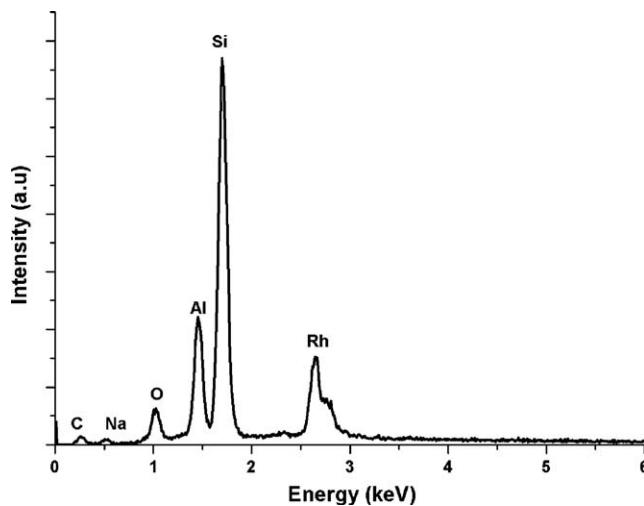


Fig. 3. The SEM-EDX spectrum of zeolite framework stabilized rhodium(0) nanoclusters with a rhodium loading of 1.2 wt.%

cages of Zeolite-Y. The X-ray photoelectron spectrum (XPS) of the zeolite framework stabilized rhodium(0) nanoclusters with a rhodium loading of 1.2 wt.% is given in Fig. 5. It shows two bands at 306.4 and 311 eV readily assigned to Rh(0) $3d_{5/2}$ and Rh(0) $3d_{3/2}$, respectively [16].

Nitrogen adsorption–desorption isotherms of Zeolite-Y and zeolite framework stabilized rhodium(0) nanoclusters samples are depicted in Fig. 6 and both of them show a Type I shape, characteristic of microporous materials [17]. The micropore volume and area were determined for Zeolite-Y and zeolite framework stabilized rhodium(0) nanoclusters by *t*-plot method [18]. On passing from Zeolite-Y to zeolite framework stabilized rhodium(0) nanoclusters, both the micropore volume (from 0.333 to 0.279 cm³/g) and the micropore area (from 753 to 632 m²/g) are noticeably reduced. This can be attributed to the encapsulation of rhodium(0) nanoclusters in the cavities of Zeolite-Y. Furthermore, no hysteresis loop was observed in the N₂ adsorption–desorption isotherm of the zeolite framework stabilized rhodium(0) nanoclusters indicating that the two steps procedure used in the nanoclusters preparation does not form any mesopores.

3.2. Catalytic activity of zeolite framework stabilized rhodium(0) nanoclusters in the hydrolysis of ammonia-borane

The zeolite framework stabilized rhodium(0) nanoclusters formed *in situ* were found to be highly active catalyst for the

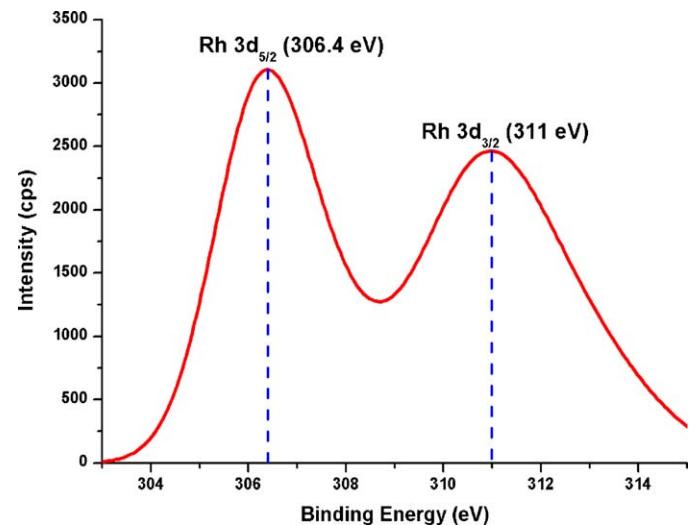


Fig. 5. X-ray photoelectron spectrum of the zeolite framework stabilized rhodium(0) nanoclusters with a rhodium loading of 1.2 wt.%

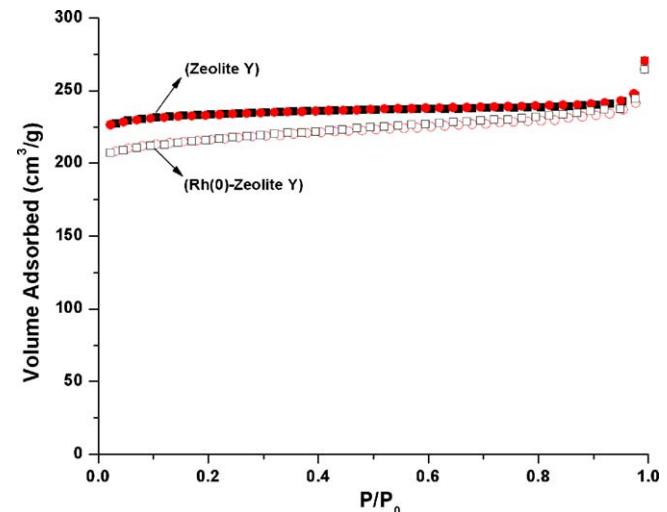


Fig. 6. Nitrogen adsorption–desorption isotherms of the host material Zeolite-Y and the zeolite framework stabilized rhodium(0) nanoclusters with a rhodium loading of 1.2 wt.%

hydrolysis of ammonia-borane. Fig. 7 shows the plots of the stoichiometric ratio of generated H₂ to H₃NBH₃ versus time during the catalytic hydrolysis of 100 mM H₃NBH₃ solution in the presence of the zeolite framework stabilized rhodium(0) nanoclus-

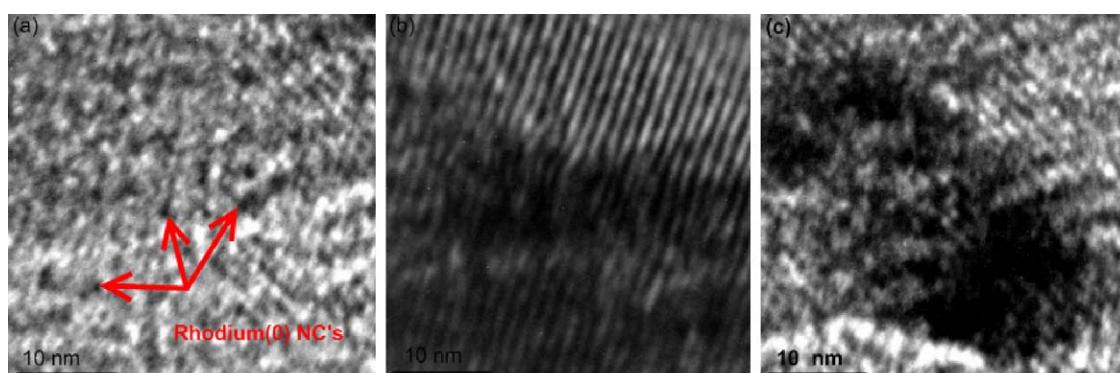


Fig. 4. (a) The high resolution TEM image of the zeolite framework stabilized rhodium(0) nanoclusters with a rhodium loading of 1.2 wt%, (b) the high resolution TEM image of the same sample with a suitable orientation of the zeolite crystal showing the distribution of rhodium(0) nanoclusters on the framework of Zeolite-Y, and (c) the high resolution TEM image of the zeolite framework stabilized rhodium(0) nanoclusters sample harvested after the fourth run.

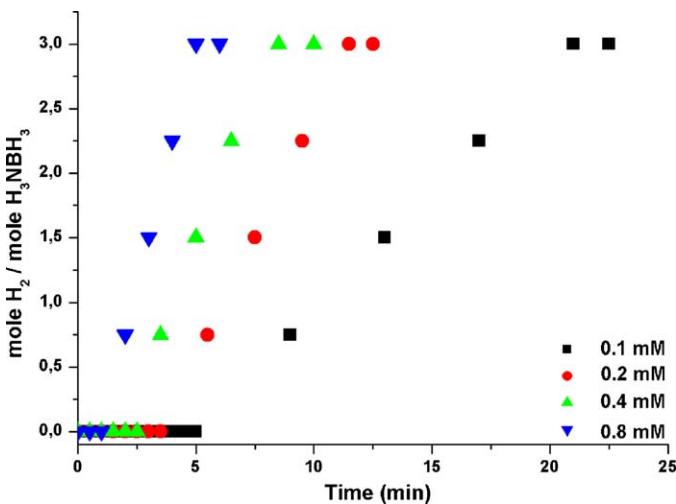


Fig. 7. Plot of mol H₂/mol H₃NBH₃ versus time (min) for the hydrolysis of ammonia-borane ([AB] = 100 mM) catalyzed by in situ formed zeolite framework stabilized rhodium(0) nanoclusters with a rhodium loading of 1.04 wt.% with different rhodium concentrations as given on the graph at 25.0 ± 0.1 °C.

ters with a rhodium loading of 1.04 wt.% in different rhodium concentrations at 25.0 ± 0.1 °C. After an induction period depending on the catalyst concentration, a linear hydrogen generation starts and continues until completion. For example, using rhodium(0) nanoclusters in 0.1 mM concentration leads to a complete hydrogen release (3.0 mol H₂/mol H₃NBH₃) within 20 min at 25.0 ± 0.1 °C. The quantity of ammonia liberated during the hydrolysis of ammonia-borane has been found to be negligible when the catalyst concentration is less than 0.06 mol% and the substrate concentration is lower than 6 wt.% [8a]. The control tests using copper(II) sulfate or acid/base indicator showed no ammonia evolution in detectable amount in the experiments.

Fig. 8 shows the stoichiometric ratio of generated H₂ to H₃NBH₃ versus time in the hydrolysis of 100 mM H₃NBH₃ catalyzed by in situ formed zeolite framework stabilized rhodium(0) nanoclusters ([Rh] = 0.2 mM) at various temperatures. It is worth noting that using zeolite framework stabilized rhodium(0) nanoclusters in 0.2 mM Rh concentration (substrate/catalyst ratio = 500) leads to a complete H₂ release (3.0 mol H₂/

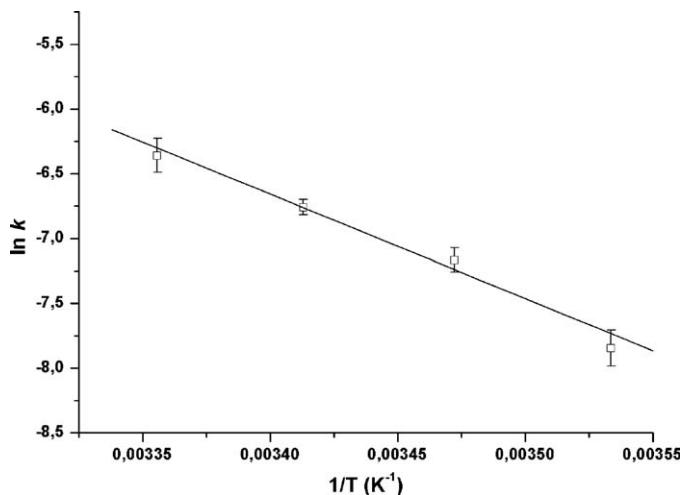


Fig. 9. Arrhenius plot for the zeolite framework stabilized rhodium(0) nanoclusters catalyzed hydrolysis of ammonia-borane, [AB] = 100 mM and [Rh] = 0.2 mM.

mol AB) within 8 min corresponding to a TOF value of 92 mol H₂/mol Rh min in air at 25.0 ± 0.1 °C. This is a remarkable TOF value since apart of Manners' colloidal Rh(0) which, however, has very low recyclability and lifetime [7b] the highest TOF known for the catalytic AB hydrolysis is 74 mol H₂/mol Pt min [19], obtained by Pt/Al₂O₃ under Ar atmosphere at 25 °C. Furthermore, the zeolite framework stabilized rhodium(0) nanoclusters show significant catalytic activity even at low temperatures (TOF = 18 – mol H₂/mol Rh min at 10 ± 0.1 °C). The rate constants of hydrogen generation from the hydrolysis of AB were measured from the linear portions of the plots given in Fig. 8 at four different temperatures in the range of 10–25 °C and used for the calculation of activation energy ($E_a = 66.9 \pm 1.3$ kJ/mol) from the Arrhenius plot as shown in Fig. 9.

3.3. Isolability and reusability of zeolite framework stabilized rhodium(0) nanoclusters in the hydrolysis of ammonia-borane

The zeolite framework stabilized rhodium(0) nanoclusters were also tested for their isolability and reusability in the AB hydrolysis. After the complete hydrolysis of 100 mM H₃NBH₃ solution catalyzed by 0.2 mM zeolite framework stabilized rhodium(0) nanoclusters at 25 °C, the catalyst was isolated as brown powders by drying in vacuum and then bottled under N₂ atmosphere. The isolated sample of zeolite framework stabilized rhodium(0) nanoclusters is redispersible in aqueous solution and yet active catalyst in the H₃NBH₃ hydrolysis. Fig. 10 shows the changes in TOF values of ZFS Rh(0) nanoclusters in the successively repeated hydrolysis, isolation and redispersion cycles at 25.0 ± 0.1 °C. They retain 70% of their initial activity at the fourth run in the hydrolysis of H₃NBH₃ with a complete release of hydrogen. This indicates that the zeolite framework stabilized rhodium(0) nanoclusters are isolable, bottleable and redispersible and yet catalytically active. In other words, they can be repeatedly used as active catalyst in the hydrolysis of H₃NBH₃. The slight decrease in catalytic activity in subsequent runs may be attributed to the passivation of nanoclusters surface by increasing boron products, e.g. metaborate, which decreases accessibility of active sites [7b,20]. Deactivation of zeolite confined rhodium(0) nanoclusters is most probably due to the blockage of entrance to the zeolite supercages by the aggregating nanoclusters. Indeed, the TEM image of the catalyst after fourth use given in Fig. 4c shows the agglomeration of nanoclusters within the zeolite.

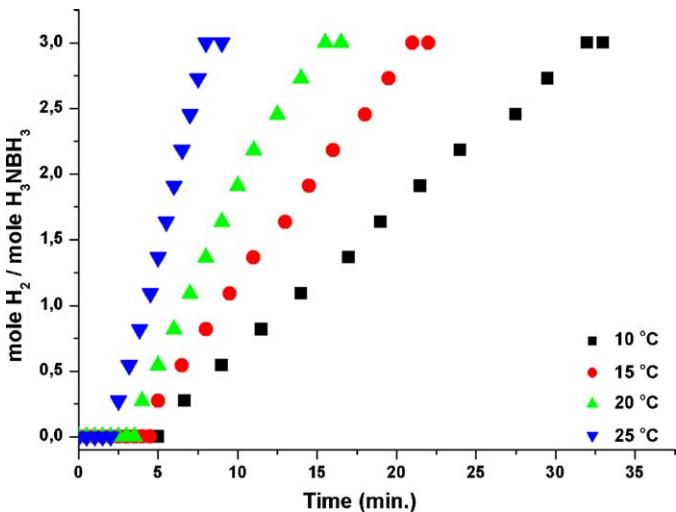


Fig. 8. Plot of mol H₂/mol AB versus time (min) for the hydrolysis of 10 mL 100 mM (30.9 mg) H₃NBH₃ catalyzed by in situ formed zeolite framework stabilized rhodium(0) nanoclusters (36 mg Rh³⁺-Y with a rhodium content of 1.2 wt.%, [Rh] = 0.2 mM) at various temperatures.

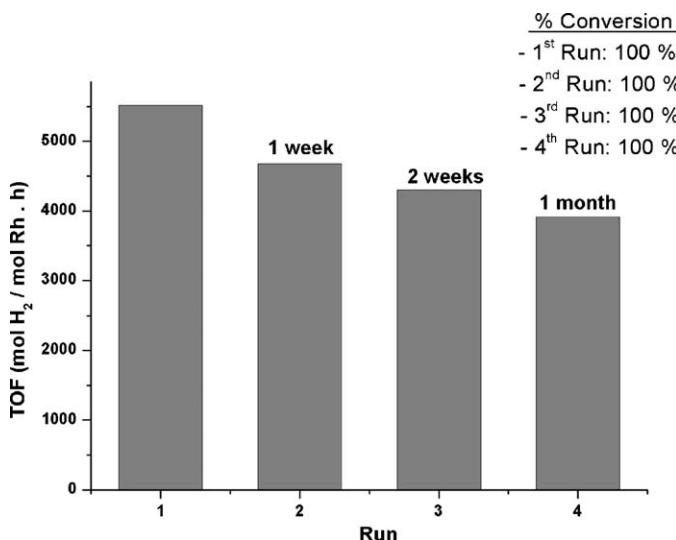


Fig. 10. Turnover frequencies (TOF) for the zeolite framework stabilized rhodium(0) nanoclusters catalyzed hydrolysis of ammonia-borane ($[AB] = 100 \text{ mM}$ and $[\text{Rh}] = 0.2 \text{ mM}$) at $25.0 \pm 0.1^\circ\text{C}$ obtained in the successive catalytic runs after isolation and redispersion.

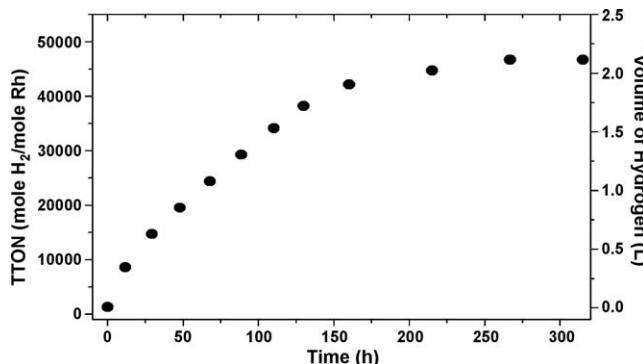


Fig. 11. Total turnover number (TTON) and volume of hydrogen versus time plot for the zeolite framework stabilized Rh(0) nanoclusters (with a rhodium content of 1.2 wt.%, $[\text{Rh}] = 1 \text{ mM}$) catalyzed hydrolysis of AB at $25.0 \pm 0.1^\circ\text{C}$.

3.4. Catalytic lifetime of zeolite framework stabilized rhodium(0) nanoclusters in the hydrolysis of ammonia-borane

More importantly, zeolite framework stabilized rhodium(0) nanoclusters provide unprecedented catalytic lifetime in the H_3NBH_3 hydrolysis at $25.0 \pm 0.1^\circ\text{C}$. Fig. 11 shows the variation in total turnover number (TTON) and volume of hydrogen gas during the H_3NBH_3 hydrolysis catalyzed by zeolite framework stabilized rhodium(0) nanoclusters formed in situ at $25.0 \pm 0.1^\circ\text{C}$. The zeolite framework stabilized rhodium(0) nanoclusters provide 47,200 turnovers over 315 h before deactivation.

4. Conclusions

In summary, our study of the preparation and characterization of zeolite framework stabilized rhodium(0) nanoclusters catalyst for the hydrolysis of H_3NBH_3 has led to the following conclusions and insights: Zeolite framework stabilized rhodium(0) nanoclusters can easily be prepared at room temperature by ion-exchange of Rh^{3+} ions with the extra framework Na^+ ions in Zeolite-Y, followed by reduction of the Rh^{3+} ions in the cavities of Zeolite-Y with ammonia-borane in aqueous solution. They were found to be highly active catalyst in the hydrolysis of ammonia-borane even at

low concentration and temperature. Moreover, the complete release of hydrogen is achieved even in successive runs performed by redispersing the zeolite framework stabilized rhodium(0) nanoclusters isolated after the previous run. Thus, they are isolable, bottleable and redispersible. When redispersed in aqueous solution of ammonia-borane, they retain essentially their initial catalytic activity. Zeolite framework stabilized rhodium(0) nanoclusters are highly active catalyst providing 47,200 turnovers in the hydrogen generation from the hydrolysis of ammonia-borane at $25.0 \pm 0.1^\circ\text{C}$ before they are deactivated.

The superb catalytic activity and outstanding catalytic lifetime of zeolite framework stabilized rhodium(0) nanoclusters result from the small size and narrow size distribution of the rhodium(0) nanoclusters which are almost half-naked interacting with internal or external surface of zeolite. In summary, we have demonstrated that zeolite framework rhodium(0) nanoclusters can easily be prepared by ammonia-borane reduction of Rh^{3+} -exchanged Zeolite-Y and exhibit superb catalytic activity and lifetime in the hydrolysis of ammonia-borane.

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